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(21) International Application Number: PCT/NL96/00039 (22) International Filing Date: 23 January 1996 (23.01.96) (30) Priority Data: <table border="0"> <tr> <td>9500118</td> <td>23 January 1995 (23.01.95)</td> <td>NL</td> </tr> <tr> <td>08/442,417</td> <td>16 May 1995 (16.05.95)</td> <td>US</td> </tr> <tr> <td>1000572</td> <td>15 June 1995 (15.06.95)</td> <td>NL</td> </tr> </table> (71) Applicant (for all designated States except US): BLYDENSTEIN-WILLINK N.V. [NL/NL]; Amaril- straat 30, NL-7554 TV Hengelo (NL). (72) Inventor; and (75) Inventor/Applicant (for US only): KROESBERGEN, Aalber- tus, Pieter [NL/NL]; Bartokpad 13, NL-3906 BZ Veenendaal (NL). (74) Agent: VAN SOMEREN, Petronella, Francisca, Hendrika, Maria; Sweelinckplein 1, NL-2517 GK The Hague (NL).		9500118	23 January 1995 (23.01.95)	NL	08/442,417	16 May 1995 (16.05.95)	US	1000572	15 June 1995 (15.06.95)	NL	(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KG, KZ, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i> <i>In English translation (filed in Dutch).</i>
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1000572	15 June 1995 (15.06.95)	NL									
(54) Title: SUBSTRATE WITH SUPER-ABSORBENT MATERIAL, METHOD FOR MANUFACTURE THEREOF AND USE											
(57) Abstract <p>The invention relates to a substrate provided with super-absorbent material to be manufactured by allowing suitable monomers to polymerize in the presence of a catalyst in order to obtain a polymer solution, adding a cross-linking agent to the polymer solution to obtain a pasty composition, subsequently applying the composition on or in a substrate and allowing the applied composition to dry and cross-link in order to obtain the substrate with the super-absorbent material. The pasty composition further contains other additives. The invention further relates to a method for manufacturing such a substrate. The substrates can be used as sheathing material in cables, in hygiene products such as baby napkins, sanitary towels and incontinence products, in or as packagings and packaging materials and in agricultural substrates. The invention also relates to said products.</p>											

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SUBSTRATE WITH SUPER-ABSORBENT MATERIAL, METHOD FOR MANUFACTURE THEREOF AND USE

The present invention relates to a substrate provided with a super-absorbent material, to a method for the manufacture thereof, a method for manufacturing the super-absorbent material, in addition to the use of the substrate in different products.

Super-absorbent materials used for a variety of applications have existed for decades. Such super-absorbent materials are capable of binding a multiple of their own weight in liquid, particularly water, sometimes up to five hundred times as much.

The super-absorbent capacity of such materials is based on swelling. The materials are at least partially cross-linked polymer chains containing a large number of COOH groups. Through contact with water or an aqueous liquid hydrogen atoms will split off and COO⁻ groups will be formed. These negatively charged carboxylate groups repulse each other, whereby the cross-linked polymer forms a three-dimensional network, in which the water molecules are as it were captured. The water molecules are held in the super-absorbent material by means of hydrogen bridges. The (partial) cross-linking of the material is essential for the effectiveness thereof, since "separate" polymer chains would simply dissolve in the liquid instead of absorbing it.

Super-absorbent materials occur as powders or fibres. The advantage of powders is that they have a markedly higher absorption capacity than fibres due to their significantly larger surface area. Super-absorbent fibres are moreover more expensive.

Powders are usually applied to a substrate, which in turn is further processed into the end product. In particular cases powders are also directly processed. The great drawback of powder however is that it causes dusting and dust nuisance both in the manufacture of substrates coated with powder and in the processing of

those substrates or the loose powders themselves. Dust nuisance is not only very unpleasant but also causes loss of material and therefore waste and is moreover bad for the health of those working with the powders.

5 It is therefore the object of the present invention to provide a substrate provided with a super-absorbent material which does not have the above stated drawbacks.

This is achieved by the invention by manufacturing the substrate by causing suitable monomers to polymerize
10 in the presence of a catalyst in order to obtain a polymer solution, adding a cross-linking agent to obtain a pasty composition, subsequently applying the composition on or in a substrate and allowing the applied composition to dry and cross-link to obtain the substrate
15 with the super-absorbent material.

In an alternative embodiment of the invention the polymer solution can also be prepared, instead of by polymerization, by dissolving already formed polymers in water or an aqueous solvent and only then adding the
20 cross-linking agent. The thus obtained composition can then again be applied to a suitable substrate.

The conventional method for preparing a super-absorbent powder consists of adding together suitable monomers and a cross-linking agent and causing these to polymerize
25 in the presence of a catalyst. The polymer obtained in this manner is gelled and dried and subsequently ground to powder. Figure 1 shows a schematic outline of the preparatory steps for manufacturing a super-absorbent powder according to the prior art.

30 In the method according to the invention however, the cross-linking step is not performed during polymerization but only thereafter. Cross-linking takes place just before, during or after the application of the mixture of the polymer solution and the cross-linking
35 agent. The material with super-absorbent properties is subsequently manufactured by drying. Figure 2 shows the process according to the invention in diagrammatic form.

The advantage of the process sequence of the present invention is that dust nuisance no longer occurs either
40 during applying of the super-absorbent material in or on

a substrate or during processing of the substrate itself. The occurrence of additional waste is also hereby prevented.

If desired, other additives can also be introduced
5 into the composition just before, simultaneously with or after addition of the cross-linking agent. The object of such additives is for instance to change the viscosity of the composition, whereby the application is facilitated, to improve the adhesion of the material to the substrate,
10 to soften the super-absorbent material, whereby the adhesion is also improved, to increase the conducting properties or to cause the composition to foam either after or during the application.

Additives which change the viscosity of the composition
15 can be chosen for instance from acrylates, polyurethane or combinations thereof. Changing the viscosity may be necessary in respect of particular methods of applying the composition to the substrate. In screen printing techniques it may be desired in particular cases for the
20 applied quantity of material not to run out or only to run out slowly. The spreading speed can be influenced by increasing the viscosity.

Additives for improving the adhesion of the super-absorbent material to the substrate are for instance
25 polyamides (PA), polyethylene (PE), ethylene vinyl acetate (EVA) or combinations thereof. These materials adhere relatively well to the commonly used substrates. By including them in the super-absorbent material the adhesion thereof can be improved. Such adhesive agents
30 can also be arranged as coating layer on the substrate prior to application of the pasty composition. The adhesion can also be enhanced by adding plasticizers. Suitable plasticizers are preferably plasticizers which are co-polymerized with the super-absorbent material so
35 that they cannot diffuse from the polymer into for instance cable insulation. Plasticizers ensure that the resulting super-absorbent material does not become too hard, whereby it could easily detach from the substrate.

To improve the conductivity of the material or end product, for instance soot (carbon) or other conducting materials can be mixed in.

Suitable foaming agents are for instance Servo
5 Amfolyt JA 140 TM, NekanilTM or combinations thereof. The advantage of an absorbent material in the form of a foam is that the surface is significantly enlarged. Hereby the swelling capacity likewise increases because the water molecules have easier access to the carboxyl groups of
10 the polymer network and these can thereby hydrolyse more rapidly.

In principle any polymer with suitable swelling properties can be processed in the manner outlined above to a pasty composition which can be applied to a
15 substrate. Particularly recommended however are polyacrylates, preferably sodium- or ammonium-neutralized acrylamides and cellulose-like polymers. A suitable cross-linking agent is added depending on the polymer. The skilled person in this field using his average
20 professional knowledge will be capable of selecting suitable cross-linking agents.

In principle any desired material can be used as substrate as long as adhesion of the super-absorbent material thereto is possible. Examples of substrates are
25 for instance fabrics, non-wovens, paper, films, for instance of plastic or metal, tape material, for instance of aluminum, or also petrojelly-like filling compounds. In addition to flat substrates filamentary or fibrous substrates can also be used.

30 The present invention further relates to a method for manufacturing a substrate provided with a coating of super-absorbent material, comprising of allowing suitable monomers to polymerize in the presence of a catalyst, adding a cross-linking agent thereto in order to obtain a
35 pasty composition, subsequently applying the composition to a substrate and allowing the applied composition to cross-link and dry to obtain the substrate with the super-absorbent material.

According to an alternative embodiment the polymer
40 solution can here also be manufactured, instead of by

polym rization, by dissolving polymer chains in water or an aqueous solvent.

There are different possibilities for applying the pasty composition to the substrate. Full surface coating results in a substantially closed layer. In principle a closed layer has a relatively low absorption capacity. For particular applications, however, such a product may be desired. In addition to surface coating, the pasty material can however also be applied by means of brushing, rolling and the like.

A third method of application is impregnation. Impregnation takes place for instance by transporting the substrate together with the pasty composition through two rollers. Depending on the wettability of the substrate, a closed layer results or accumulations of the composition form locally. The latter occurs particularly when a hydrophobic substrate is used.

A third possibility of applying the pasty composition is by means of screen printing techniques. The material is herein applied to the substrate through a template. The form, distribution and dimensions of the openings in the template determine the resulting pattern on the substrate.

The properties of the swelling material depend on a number of factors. Thus both the ratio between temperature (during application and drying) and the drying time as well as the viscosity of the composition are important for the adhesion to the substrate and for the swelling capacity. Cross-linking agents are generally active at relatively high temperatures and in aqueous environments. In the ideal case, the cross-linking should take place at between 150 and 200°C, preferably about 175°C, and at a pressure such that water has not yet evaporated. In practice however, atmospheric pressure and a temperature of about 175°C are often chosen. It has been found according to the invention that with a drying time of between 1 and 3 minutes at 175°C an absorbent material with good properties is obtained. The time and temperature can however vary depending on the ratio between the

quantities of acrylate and cross-linking agent and the viscosity of the mixtur .

It has been found that in the first drying run the evaporation of the cross-linking agent must be prevented
5 as far as possible. This can be achieved by operating with the lowest possible air circulation.

In addition, the form in which the super-absorbent material is applied is also important for the absorption properties. With powders it has been found in practice
10 that particles with a diameter of between about 100 and 200 μ have the best absorption properties. According to the invention the composition is therefore preferably applied in the form of discrete, substantially semi-spherical islets with a diameter of between about 100 and
15 200 μ . Depending on the application the islets may however also have greater or smaller diameters, for instance between 10 and 1000 μ , preferably between 50 and 500 μ .

The distribution of the islets on the substrate can be random or in accordance with a determined pattern. In
20 addition, a greater number of islets or islets with a different diameter may be arranged at determined locations on the substrate in order to locally increase the absorption capacity. This is important for instance when the product is used in hygiene products such as baby
25 napkins and sanitary towels. A skilled person will be able to ascertain by means of simple tests which pattern is most suitable for a particular application.

The absorption capacity of the substrate depends on the quantity of super-absorbent material applied. In the
30 present case 30 g per m^2 would already provide sufficient absorption. Starting from this given information, it can be calculated how much material must applied per islet of 200 μ and what the distance between the islets must be, for instance by means of the following calculation:

35 - the volume of an islet is:

$$\frac{2}{3} \pi r^3 = \frac{2}{3} * 3.14 * (0.002)^3 = 1.7 \cdot 10^{-8} \text{ dm}^3$$

- the specific weight is set at:

$$1 \text{ kg/m}^3$$

- the weight of one semi-sphere is then:

40 $1.7 \cdot 10^{-5} \text{ g}$

- a weight of 30 g/m^3 then results in:
 $1.75 \cdot 10^6$ semi-spheres
- the diameter surface of one semi-sphere is:
 $3.14 \cdot 10^{-8} \text{ m}^2$
- 5 - the total surface of the dots together is:
 0.0553 m^2
- the distance between the dots amounts to:
 $8 \cdot 10^{-6} - 2 \cdot 10^{-6} = 600 \mu$

10 The quantity of material to be applied is determined by the form and dimensions of the openings in a template. In the case of semi-spherical islets the material will preferably be applied in the shape of a cylinder and will then assume the ideal semi-spherical shape by flowing out slightly.

15 It has been found that super-absorbent material applied with a CP30 template has a swelling capacity of about 1 mm per 10 g/m^2 in tap water. A full surface coated layer of absorbent material has for instance a swelling capacity of about 0.2 mm per 10 g/m^2 (in tap water with an
20 average conductivity).

25 The substrate with the super-absorbent material according to the invention can in principle be used in any field in which at the moment super-absorbent powders and fibres and substrate materials provided with super-absorbent powders and fibres are also used.

30 An example of a particularly advantageous application is the use of the substrate as sheathing material in the cable industry. Sheathing material is used for electricity cables and data cables and has a number of functions. It serves for instance to embed the conducting part of the cable and to form a barrier to the environment (the so-called bedding function). In addition, sheathing material is used to hold together the components of a cable (so-called binding). Furthermore, determined components of a cable must be mutually separated
35 (separation). Sheathing material is also used for this purpose. An important fourth and final function is so-called water-blocking, which must prevent water penetrating to the core in transvers as well as longitudinal
40 direction. The sheathing material according to the inven-

tion is particularly suitable for this latter function. Heretofore petrojelly-like compounds or substrate materials coated with a super-absorbent powder have been used for this purpose. Processing of petrojellies is far
5 from agreeable and causes a considerable degree of smearing, leakage of the jellies etc. during manufacture of the cables as well as during connection thereof. The drawbacks of powdery super-absorbent materials are already described above. The substrate according to the
10 invention is particularly suitable as water-blocking material in cables.

Super-absorbent materials are in addition also much used in hygiene products such as baby napkins, sanitary towels and incontinence products. In the manufacture of
15 such products and the use thereof the drawbacks of the powders used heretofore are prevented by using a substrate according to the invention.

Another application of the substrate according to the invention lies in the field of agriculture, where
20 moisture-regulating conditions can be provided, for instance in agricultural substrates, by means of the super-absorbent properties of the material.

The material can also be used in the packaging industry. In products which must be stored absolutely
25 moisture-free, bags of silica gel are often co-packed. The invention enables packaging of the product for instance directly in a substrate provided with a super-absorbent material.

In the present application the following terminology
30 is used. By "polymer solution" is understood a polymer-containing liquid phase before addition of a cross-linking agent. By "composition" is understood the polymer solution after addition of the cross-linking agent, prior to as well as after the application thereof to a
35 substrate, optionally after cross-linking but still before drying. "Absorbent material" designates the composition after cross-linking and drying.

Th inv ntion will be further elucidated on the basis of the accompanying example, which is only given

however by way of illustration and is not intended to limit the invention in any way whatsoever.

EXAMPLE

The super-absorbent composition according to the invention was prepared from two components. Component 1 consists of an aqueous solution of a pre-cross-linked poly(meth)acrylic acid, which can be partially present in the form of a salt. The counter-ions can in that case be sodium, potassium or ammonium. In addition, the solution can optionally contain acrylamide as co-monomer. The monomer containing the carboxyl group ((meth)acrylic acid) must however always be present in excess.

The second component is the actual reactive cross-linking agent, which preferably contains two functional groups which are capable after thermal excitation of reacting in a short time with carboxylate or carbonic acid functional groups.

Shortly before application of the mixture to the substrate, component 2 in a quantity of 0.1-5% by weight, preferably 0.5-3% by weight related to the total quantity of component 1, is added to component 1 (95-99.9% by weight) and mixed homogeneously therewith.

The mixture is applied to a suitable substrate by means of screen printing techniques with a screen having a mesh width of 500-1000, preferably 745 μ in order to obtain a regular pattern of islets with a diameter of 100-500, preferably 250 μ and an open area of 5-20, preferably 13%. After printing, the substrate with the mixture thereon is dried in order to cause the cross-linking process to take place. The thus obtained product has a swelling capacity of 1 mm at an application of 9 g/m² (dry).

The present invention provides a new substrate which is provided with a super-absorbent material and which during manufacturing and processing displays none of the drawbacks of the substrates coated with conventionally used super-absorbent powders. A new method is further provided for manufacturing the substrate and for the

preparation. The substrate can take different forms and be used for a large number of applications.

CLAIMS

1. Substrate provided with super-absorbent material obtainable by allowing suitable monomers to polymerize in the presence of a catalyst in order to obtain a polymer solution, adding a cross-linking agent to the polymer solution to obtain a pasty composition, subsequently applying the composition on or in a substrate and allowing the applied composition to dry and cross-link in order to obtain the substrate with the super-absorbent material.

2. Substrate as claimed in claim 1, characterized in that the pasty composition further comprises other additives chosen from agents for changing the viscosity of the composition, agents for improving the adhesion of the super-absorbent material to the substrate, agents for softening the super-absorbent material, agents for making the composition conductive, agents for causing the composition to foam after or during application.

3. Substrate as claimed in claim 2, characterized in that the agents for changing the viscosity of the composition are chosen for instance from acrylates, polyurethane or combinations thereof.

4. Substrate as claimed in claim 2, characterized in that the agents for improving the adhesion of the super-absorbent material to the substrate are chosen from polyamide (PA), polyethylene (PE), ethylene vinyl acetate (EVA) or combinations thereof.

5. Substrate as claimed in claim 2, characterized in that the agents for softening the super-absorbent material are plasticizers which co-polymerize in the polymer.

6. Substrate as claimed in claim 2, characterized in that the agents for causing the composition to foam after or during application are chosen from Servo Amfolyt JA 140 TM, NekanilTM or combinations thereof.

7. Substrate as claimed in any of the claims 1-6, characterized in that the cross-linking agent contains two functional groups which are capable after thermal

excitation of reacting in a short time with carboxylate or carbonic acid functional groups.

8. Substrate as claimed in any of the claims 1-7, characterized in that the composition contains soot
5 (carbon) to make the composition conductive.

9. Substrate as claimed in any of the foregoing claims, characterized in that the composition is located on the substrate in the form of discrete, substantially semi-spherical islets with a diameter of between 100 and
10 200 μ .

10. Substrate as claimed in any of the foregoing claims, characterized in that instead of by polymerization the polymer solution is prepared by dissolving an already formed polymer in water or an aqueous solvent.

11. Substrate provided with a plurality of discrete, substantially semi-spherical islets of a super-absorbent material with a diameter between 100 and 200 μ .
15

12. Substrate as claimed in any of the claims 1-11, characterized in that the super-absorbent material is a cross-linked polyacrylate, polyamide, cellulose-like polymer or a combination thereof.
20

13. Substrate as claimed in any of the claims 1-12, characterized in that the substrate is a fabric, non-woven, paper, film, aluminum tape, fibre or petrojelly-like filling compound.
25

14. Substrate as claimed in any of the claims 1-12, characterized in that the pasty composition consists of 95-99.9% by weight of an aqueous solution of pre-cross-linked poly(meth)acrylic acid and 0.1-5, preferably 0.5-3% by weight of a cross-linking agent.
30

15. Method for manufacturing a substrate provided with a coating of super-absorbent material, comprising of allowing suitable monomers to be polymerized in the presence of a catalyst, adding thereto a cross-linking agent in order to obtain a pasty composition, subsequently
35 applying the composition on a substrate and allowing the applied composition to dry in order to obtain the substrate with the super-absorbent material.

16. Method as claimed in claim 15, characterized in that instead of by polymerization the polymer solution is
40

prepared by dissolving an already formed polymer in water or an aqueous solvent.

17. Method as claimed in claim 15 or 16, characterized in that the composition is applied to the substrate by means of full surface coating.

18. Method as claimed in claim 15 or 16, characterized in that the composition is applied to the substrate by means of impregnating the substrate with the composition between two rollers.

19. Method as claimed in claim 15 or 16, characterized in that the composition is applied to the substrate by means of screen printing techniques.

20. Method as claimed in claim 19, characterized in that in the screen printing technique use is made of a template with a form, size and distribution of the openings such that the composition is applied to the substrate in the form of discrete islets.

21. Method as claimed in claim 20, characterized in that the form of the template openings is chosen such that the resulting islets are substantially semi-spherical.

22. Method as claimed in claim 21, characterized in that the diameter of the semi-spherical islets lies between 10 and 1000 μ , preferably between 50 and 500 μ , most preferably between about 100 and 200 μ .

23. Method for manufacturing a paste of super-absorbent material, comprising of allowing suitable monomers to polymerize in the presence of a catalyst and subsequently adding thereto a cross-linking agent and, if desired, other additives.

24. Method for manufacturing a paste of super-absorbent material, comprising of dissolving a polymer in water or an aqueous solvent and subsequently adding thereto a cross-linking agent and, if desired, other additives.

25. Substrate as claimed in any of the claims 1-14 for use as sheathing material in cables.

26. Substrate as claimed in any of the claims 1-14 for use in hygiene products such as baby napkins, sanitary towels and incontinence products.

27. Substrate as claimed in any of the claims 1-14 for use in or as packagings and packaging materials.

28. Substrat as claimed in any of the claims 1-14 for use in agricultural substrates.

5 29. Cable provided with a sheathing material which is formed from a substrate as claimed in any of the claims 1-14.

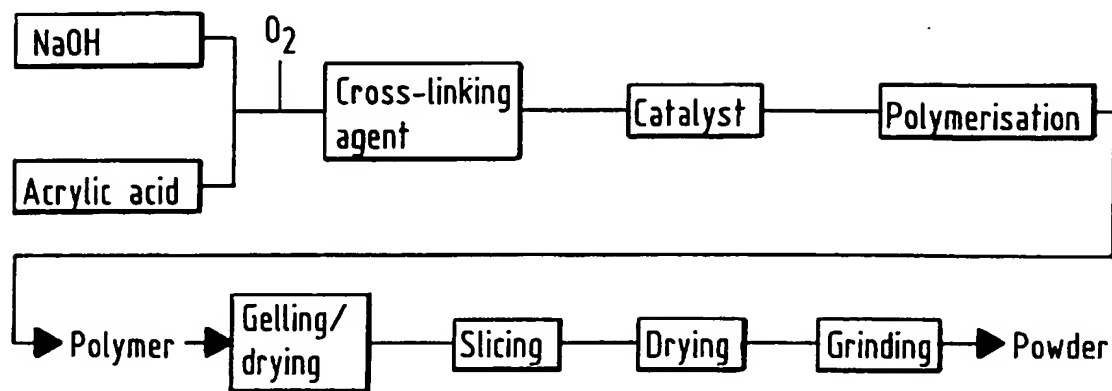
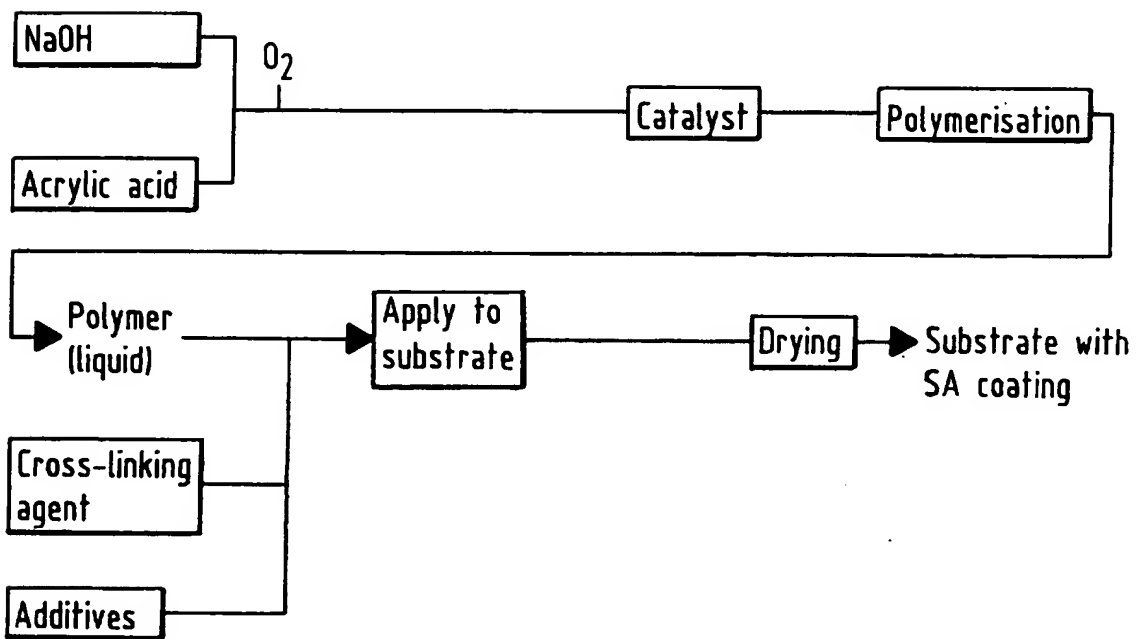
10 30. Hygiene product, such as baby napkin, sanitary towel and incontinence product, provided with a substrate as claimed in any of the claims 1-14.

31. Hygiene products provided with absorption means which are formed by or at least partly consist of a substrate as claimed in any of the claims 1-14.

15 32. Packaging material which is formed by or at least partly consists of a substrate as claimed in any of the claims 1-14 or which comprises such a substrate.

33. Agricultural substrate formed by or at least partly consisting of a substrate as claimed in any of the claims 1-14.

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FIG. 1FIG. 2

INTERNATIONAL SEARCH REPORT

Internat. Application No

PCT/NL 96/00039

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08J7/04 D06M15/263 A61L15/00 B32B33/00 H01B7/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J D06M A61L B32B H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 154 898 (BURKHOLDER NELSON D JR) 15 May 1979	1,7, 12-15, 17,18, 23,26, 30,31
Y	see the whole document	2-5,8, 19,20, 25, 27-29, 32,33
X	US,A,4 017 653 (GROSS JAMES R) 12 April 1977 see the whole document	10,14, 16,24, 30,31

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

21 May 1996

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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